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13. ABSTRACT (Maximum 200 words)  The aim of this project was to investigate the use of tethered chains to increase the energy absorption capability of the fiber-matrix interface, and thereby enhance the ballistic protection properties of fiber composites. The governing strategy was to tailor the discontinuous fiber-matrix interface so as to introduce a volume of interaction capable of providing additional, molecular-level energy dissipation mechanisms to the composite during impact. This was accomplished by covalently tethering compatible polymer chains to the surface of the reinforcing phase, while leaving the other end of the chains free to interact with the adjacent matrix phase. The project encompassed a spectrum of experimental work involving synthetic preparation of end-functional polymer chains, derivitization of the glass surface for chain attachment, characterization of the resulting tethered layer, and mechanical evaluation of both isolated and distributed interfaces at low and high rates. The effectiveness of the tethered chain concept for the improvement of impact performance was clearly demonstrated for isolated interfaces at both low ( $\sim 10^{-4}$ s <sup>-1</sup> ) and high (1 s <sup>-1</sup> ) test rates. High rate compressive tests performed on composites containing distributed interfaces showed no improvement in performance, however. This latter result was attributed to the matrix-dominated nature of impact failure encountered during the compressive testing.				
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**COMPOSITE ARMOR PERFORMANCE ENHANCEMENT BY TETHERED  
POLYMER CHAINS AT THE FIBER-MATRIX INTERFACE**

**FINAL PROGRESS REPORT**

**AUTHORS: D.S. KALIKA AND L.S. PENN**

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**AUTHORS: D.S. KALIKA AND L.S. PENN**

**STATEMENT OF THE PROBLEM STUDIED**

The aim of this project was to investigate the use of tethered chains to increase the energy absorption capability of the fiber-matrix interface, and thereby enhance the ballistic protection and impact properties of fiber composites. The governing strategy was to tailor the fiber-matrix interface so as to introduce at the interface a volume of interaction capable of providing additional, molecular-level energy dissipation mechanisms to the composite during impact. This was accomplished by covalently tethering compatible polymer chains to the surface of the reinforcing phase, while leaving the other end of the chains free to interact with the adjacent matrix phase. This strategy, with its focus on the interface, is uniquely promising because the interface is well-distributed throughout the composite, and because a given volume of composite possesses a large amount of interfacial area.

In order to objectively assess the efficacy of the tethered chain concept for the improvement of impact performance in fiber composites, special attention must be given to the preparation and characterization of the modified interface, as well as to the mechanical testing of the resulting composite. The investigation described here was comprised of three phases: (i) development of the chemical protocols required for the preparation of end-functional polymer chains and for their covalent attachment to the fiber surface; (ii) rigorous characterization of the physical and chemical nature of the tethered layer, and prediction of tethered chain conformation at the interface; (iii) mechanical testing of both the isolated interface and distributed interface over a range of timescales. The execution of this program has led to fundamental insights as to the molecular phenomena involved in the chain tethering process and the resulting characteristics of the tethered chain layer. In addition, new mechanical testing protocols have evolved from this work as a result of our efforts to achieve a unified assessment of the benefits of the tethered chain strategy.

**SUMMARY OF THE MOST IMPORTANT RESULTS**

As outlined above, this project encompassed a spectrum of experimental work involving synthetic preparation of end-functional polymer chains, derivitization of the glass surface for chain attachment, characterization of the resulting tethered layer, and mechanical evaluation of both isolated and distributed interfaces at low and high test rates. The details of this work and the corresponding results have been described in published

papers, and manuscripts currently under preparation; an overview of the entire project is contained in a paper recently prepared for the Proceedings of the First Korea-U.S. Workshop on Composite Materials (Seoul National University), "*Interfacial Tailoring for Impact Resistance and Crashworthiness in Composites*". In this report, only the most important results from each phase of the work are highlighted. For additional details, the reader is referred to the source publications.

*(a) Preparation of End-Functional Polymer Chains & their Attachment to the Glass Surface*

The polymer chains selected for tethering were end-functional polysulfone, which were used in conjunction with thermoplastic polysulfone matrix and glass fiber reinforcement. Preparation of amine-terminated polysulfone chains was accomplished by step polymerization procedures reported in the literature, and was based on the inclusion of 4-aminophenol as an end-capping reagent. Target degree of polymerization for the end-functional chains was in the range of  $N = 20$  to  $60$ . The actual polymer molecular weight that was achieved was determined using a combination of size exclusion chromatography and end group analysis (*i.e.* non-aqueous titration); the latter method also established the nature of the polymer chain ends.

The glass surface was epoxidized in preparation for tethered chain attachment by reaction with 3-glycidoxypropyltrimethoxysilane (Aldrich Chemical). Quantitative assessment of the reactive sites was accomplished by means of colorimetric analysis using 4,4'-dimethoxytrityl chloride dye coupling reagent:  $2.7$  reactive sites per  $\text{nm}^2$  were measured, a value consistent with the theoretical maximum of native hydroxyls present on the glass surface. The amine-terminated polysulfone was attached to the derivitized glass under anhydrous conditions followed by vigorous extraction to remove any non-tethered chains. Tethered chains were introduced on the surface of E-glass fiber, and also on solid and hollow glass beads.

In order to monitor the dispersity characteristics of the incipient tethered layer, the heterogeneous reaction kinetics associated with chain tethering were followed by periodic sampling of the reaction mixture. Aliquots removed from the reaction vessel were analyzed by size exclusion chromatography so that possible chain length effects during the course of chain tethering could be assessed. It was observed that the average molecular weight of the developing tethered layer increased with grafting time. This indicates a preferential attachment of shorter chains to the glass surface during the early stages of tethering, and suggests sequential addition as a way to control length and dispersity of the tethered chain layer.

*(b) Characterization of the Tethered Layer*

The tethered chain attachment density was quantified using thermogravimetric analysis (TGA). In order to increase the sensitivity inherent to this approach, polymer chains were tethered to hollow glass beads that provided a specific surface area of  $1.3 \text{ m}^2/\text{gm}$ , that is ten times greater than the specific surface area of glass fiber. By the use of proper

controls, it was possible to distinguish the mass loss associated with the decomposition of the tethered polymer chains from losses associated with water and thermal decomposition of silane; these events were confirmed by the use of TGA-mass spectrometry. The surface attachment density was observed to be a strong function of tethered chain molecular weight, and decreased with increasing tethered chain length in agreement with theory. Tethered chain attachment density was in the range of  $\sim 0.10$  chains per  $\text{nm}^2$  (longest chains) to 1.3 chains per  $\text{nm}^2$  (shortest chains).

A theoretical phase diagram was used to predict the conformation of the tethered chains as a function of their surface attachment density and the length of the surrounding matrix chains. At high attachment densities, the tethered chains are forced into a stretched, brush-like conformation that tends to exclude the matrix chains and thereby reduces the extent of interaction between the tethered layer and the matrix. At lower attachment densities, the tethered chains mix more readily with the surrounding matrix chains. Low-rate mechanical tests on the isolated interface revealed a correlation between the tethered chain conformation and interfacial performance (*see below*), with higher interfacial toughness observed for specimens wherein mixing of the tethered chain layer with the matrix was predicted.

### *(c) Mechanical Testing of the Isolated Interface*

#### *(i) Low rate testing*

The performance of the isolated fiber-matrix interface was evaluated at low rates by two established testing methods: the single fiber pull-out test and the single fiber fragmentation test. In the pull-out test, a droplet of polymer was applied to the surface of the fiber, and the required debond load was measured as a function of droplet (interface) length at a strain rate on order of  $10^{-4} \text{ s}^{-1}$ . By recording data over a range of droplet lengths, an upper bound of performance was established for each interface. The presence of the tethered chains led to a statistically significant enhancement in interfacial performance as compared to the epoxidized glass surface without tethered chains; interfacial toughness increased with increasing tethered chain length, and correlated with the conformation of the tethered chains (mixed vs. stretched, unmixed) as predicted by the phase diagram.

For the fiber fragmentation test, a single glass fiber was embedded in polysulfone matrix, which was machined into a dogbone shape. Upon imposition of (low-rate) load, the fiber fragmented, with the average fragment length in the gage section indicative of interface quality. The better the interface, the shorter the resulting fragments. Representative data for the single fiber fragmentation test are provided in Table 1, with values of fragment length reported for both the epoxidized fiber (control), and glass fiber with long tethered chains (chain  $M_w \sim 32,500$ ). The fragment length was markedly shorter for the interface with the tethered chains, reflecting improved performance as compared with the control. This result was consistent with the data obtained from the single fiber pull-out test.

**Table 1:** Single fiber fragmentation results obtained at low and high rates.

<b>Surface</b>	<b>Fragment Length, ± 1 std. Deviation (mm) <i>Low rate</i></b>	<b>Fragment Length, ± 1 std. Deviation (mm) <i>High rate</i></b>
Epoxidized Glass	0.911 ± 0.172	1.692 ± 0.290
Tethered Chains ( $M_w \sim 32,500$ )	0.699 ± 0.062	1.188 ± 0.238

(ii) High rate testing

In order to assess the effectiveness of tethered chains for the enhancement of energy absorption under impact conditions, it was necessary to pursue mechanical testing of the isolated interface at higher rates. A new version of the single fiber fragmentation test was developed for this purpose, and was based on a combination of the traditional fiber fragmentation test and the tensile impact test (ASTM D1822). By performing the fragmentation test in a standard tensile impact apparatus, it was possible to obtain strain rates on the order of  $1 \text{ s}^{-1}$ , *i.e.* 3 to 4 orders of magnitude higher than the (low rate) tests described above. Results for the high rate fiber fragmentation test are reported in Table 1, and again show improved performance for the interface containing tethered chains versus the epoxidized control. It thus appears that the additional energy dissipation mechanisms provided by the tethered chains operate not only at low rate but also at impact rate ( $\sim 1 \text{ s}^{-1}$ ), a result that has important implications for the improvement of impact resistance in fiber composite materials.

(d) *Mechanical Testing of the Distributed Interface*

In addition to mechanical tests based on isolated interfaces, a program of high rate testing was undertaken for samples containing distributed interfaces. Specifically, polysulfone cylinders were prepared with glass bead loading of twenty percent by volume. Two types of glass beads were used: glass beads with epoxidized surface (control), and glass beads with tethered chains. The glass beads were distributed in the matrix using solution-based methods, and test cylinders were formed by consolidation at  $250^\circ\text{C}$ . An independent series of thermogravimetric studies was performed in order to establish the integrity of the tethered layer over the thermal history inherent to sample preparation.

High rate compressive testing was performed utilizing equipment available at the Army Research Laboratory (Aberdeen Proving Ground) under the direction of Dr. Robert Lieb. This apparatus was capable of providing a compression rate of 2 meters per second (average strain rate  $\sim 160 \text{ s}^{-1}$ ); stress-strain data were obtained to failure at  $21^\circ\text{C}$ .

Examination of the stress-strain curves for the tethered chain specimens and the control revealed no significant difference in the performance of the two types of specimens; *i.e.* the presence of the tethered chains appeared to provide no improvement in toughness under these particular test conditions.

There are two possible explanations for the above result. One is that the dissipation mechanisms associated with the tethered chains did not have time to operate at the extremely high rate of this test. Another is that the compression loading mode and the spherical geometry of the glass reinforcement interacted to make the failure process matrix-dominated, and thereby insensitive to the interface. We would argue that the second explanation is the correct one. Although the test rate is high and might preclude viscous dissipation mechanisms, the test time is still longer than that needed for chain scission (picoseconds). Also, failed experimental and control specimens displayed extremely high amounts of matrix fracture and macroscopic matrix deformation. This behavior is consistent with a failure process that is matrix-dominated. It also suggests that the test was not interface sensitive, and that another type of test configuration should be considered.



## LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS:

M.J. Greenfield, D.S. Kalika, and L.S. Penn, "*Toughening of Impenetrable Interfaces by Tethered Chains I: Evaluation of the Isolated Interface at Low Strain Rates*" (in preparation).

M.J. Greenfield, D.S. Kalika, and L.S. Penn, "*Toughening of Impenetrable Interfaces by Tethered Chains II: Evaluation of Isolated and Distributed Interfaces at High Strain Rates*" (in preparation).

T.F. Hunter, D.S. Kalika, and L.S. Penn, "*Attachment Characteristics of End-Functional Polymer Chains at an Impenetrable Interface*" (in preparation).

M.J. Greenfield, A. Pedicini, and L.S. Penn, "*Development of a Single Fiber Fragmentation Test for High Strain Rates*", International Journal of Adhesion & Adhesives (in review, 1998).

L.S. Penn and T.F. Hunter, "*A Method for Evaluation of Molecular Weight Distribution of Polydisperse Grafted Layers*", J. Polymer Science: Chemistry Edition, 37, 1 (1999).

J.B. Ibieta, D.S. Kalika, and L.S. Penn, "*Chain End Analysis of Bisphenol A Polysulfone and Its Relation to Molecular Weight*", J. Polymer Science: Chemistry Edition, 36, 1309 (1998).

L.S. Penn and R. Lin, "*Use of a Phase Diagram to Predict and Interpret Behaviour at Interfaces in Immiscible Polymer Blends*", International Journal of Adhesion & Adhesives, 17, 79 (1997).

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## PROCEEDINGS AND ABSTRACTS:

L.S. Penn, D.S. Kalika, M.J. Greenfield, J.B. Ibieta, T.F. Hunter, and R. Lin, "*Interfacial Tailoring for Impact Resistance and Crashworthiness in Composites*" Proceedings of the First Korea-U.S. Workshop on Composite Materials; Seoul National University, 1998.

M. Greenfield, A. Pedicini, D. Kalika and L. Penn, "*A High-Rate Test for the Isolated Fiber-Matrix Interface*", 21st Annual Meeting of the Adhesion Society, Savannah GA, 1998.

L.S. Penn, D.S. Kalika, M.J. Greenfield, and A. Pedicini, "*Evaluation of the Fiber-Matrix Interface at High Rates*". Materials Research Society, Fall Meeting, Boston, 1997.

L. Penn, D. Kalika, R. Lin, M. Greenfield, R. Quirk and J. Kuang, "*Enhancement in Toughness of Impenetrable Interfaces By Tethered Polymer Chains*". Materials Research Society, Fall Meeting, Boston, 1996.



## PROCEEDINGS AND ABSTRACTS (cont.)

L. Penn, D. Kalika, R. Lin, J. Ibieta, M. Greenfield, R. Quirk, and J. Kuang, "*Toughening of Impenetrable Interfaces by Tethered Polymer Chains*", Proceedings of the American Chemical Society, Div. of Polymer Chemistry, 37 (2), 47 (1996).

L. Penn, D.S. Kalika, and R. Lin, "*Tethered Chains at Impenetrable Interfaces*," Gordon Res. Conf. Science of Adhesion, Tilton, NH, 1996.

L. Penn and D.S. Kalika, "*Tethered Chains as a Toughening Strategy*," Army Research Office Workshop on Hierarchical Structures, Charleston, SC, 1995.

R. Lin, J. Ibieta, D.S. Kalika, and L.S. Penn, "*Enhancement of Impenetrable Interfaces by Tethered Polymer Chains*," The Intersociety Polymer Conference, Baltimore, 1995.

R. Lin, D.S. Kalika, H. Wang, and L.S. Penn, "*Preparation and Performance of Tethered Chains at Impenetrable Interfaces*", Materials Research Society, Fall Meeting, Boston, 1994.

R. Lin, D.S. Kalika, and L.S. Penn, "*Tailoring the Interface with Tethered Chains*", Annual Meeting of the Adhesion Society, Orlando, 1994.

## **LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL**

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### **Post-Doctoral:**

**Dr. Hua Wang** (Fall, 1994)

### **Ph.D. Students:**

**Mark Greenfield**, *"High-Rate Investigation of Energy Dissipation in Two-Phase Materials with Tailored Interfaces."* Degree expected June, 1999.

**R. Lin**, *"Toughness Enhancement of an Impenetrable Interface by Tethered Polymer Chains"*. Ph.D, August 1996.

### **M.S. Students:**

**Talmadge Hunter**, *"Attachment Characteristics of End-Functional Polymer Chains at an Impenetrable Interface"*. Degree expected December, 1998.

**J.B. Ibieta**, *"Characterization Method for the Analysis of Multiple Functional-Ended Polysulfone"*. M.S., May 1997.

### **Undergraduate Students:**

**Angelo Pedicini**; B.S. in Materials Science & Engineering, May, 1998.

## **REPORT OF INVENTIONS**

None